Determination of the Coefficient of Inter-Diffusion of Gases and the Velocity of Ions under an Electric Force, in Terms of Mean Free Paths.

By John S. Townsend, F.R.S., Wykeham Professor of Physics, Oxford.

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1. The properties of gases which depend on the velocity of agitation of molecules and the lengths of their free paths may easily be expressed in terms of the mean velocity of agitation and the mean free path when certain assumptions are made in order to simplify the investigations. The expressions thus found on the principles of the kinetic theory are in good agreement with the experimental results in most cases, but the formulæ that have been obtained for the coefficient of inter-diffusion of gases and the velocity of particles acted on by an external force are not so satisfactory.

The equations of motion of two inter-diffusing gases have been given by Maxwell, and it may be shown from these that the exact value of the ratio of the coefficient of diffusion of ions to the velocity under unit electric force is $\mathrm{N}e/\Pi$, where N is the number of molecules per cubic centimetre of a gas at pressure Π, and e the charge on an ion. The method adopted by Maxwell is perfectly general, there are no assumptions made as to the distribution of the velocities of agitation, and no particular definition of a collision or a free path is involved, so that there can be little doubt as to the accuracy of the result.

When, however, the coefficient of diffusion in terms of the mean free path and velocity of agitation that is usually given is compared with the velocity under an electric force expressed in terms of the same quantities the ratio obtained is about one-half the above value.

It is interesting, therefore, to examine these formulæ and to see how the error arises, for when the correct expressions for the rate of diffusion and the velocity under an electric force are found, it is easy to see that Maxwell's equations follow immediately from them. These investigations have been made on the supposition that the molecules travel with a constant velocity of agitation, which is the same as the mean value of that velocity.

The investigations are much simplified when this assumption is made, and no serious error is introduced, since the velocity of a molecule seldom differs by much from the mean value as is shown by Maxwell's law of distribution of the velocities, from which it may be seen that the ratio of the mean velocity to the square root of the mean square of the velocity is 12/13. A somewhat larger error would be introduced if calculations were made on the supposition that the free paths were all equal to the mean free path. It is unnecessary, however, to introduce this simplification, as it is easy to take into consideration variations in the lengths of the free paths.

For if l is the mean length of a large number N of free paths of a molecule or the mean distance that a large number of particles will travel before they collide; then the number of paths n that exceed a distance x is $n = \mathrm{N}e^{-x/l}$. The mean square of the paths is

$$\int_0^\infty x^2 e^{-x/l}\frac{dx}{l} = 2l^2,$$

or twice the square of the mean free path.

This result is frequently neglected, and in many text books it is stated that the values of the coefficients, such as that of viscosity $\eta = \frac{1}{3}mnl\mathrm{V}$, can be obtained on the supposition that the free paths are all equal to the mean free path. It is obvious that the coefficient of viscosity would be $\frac{1}{6}mnl\mathrm{V}$ if all the molecules traversed paths of length l with a velocity V.

As regards the coefficient of inter-diffusion of two gases considerable difference of opinion has been expressed as to the correct value of this coefficient. The expression usually given is $\frac{1}{3}(\mathrm{N}_1\mathrm{L}_2\mathrm{V}_2+\mathrm{N}_2\mathrm{L}_1\mathrm{V}_1)/\mathrm{N}$, N_1 and N_2 being the numbers of molecules per cubic centimetre of the two gases, L_1 and L_2 the mean free paths of the molecules, V_1 and V_2 their velocities of agitation. The numerical factor $\pi/8$ is sometimes given instead of $\frac{1}{3}$. The objection to this formula is that it gives different values for the diffusion when the proportion of the two gases $\mathrm{N}_1/\mathrm{N}_2$ is altered, which is contrary both to experimental evidence and also to the result of the simpler investigation by which Maxwell found the equations of motion of two inter-diffusing gases.

This difficulty has been avoided by Maxwell by assuming that the encounters between molecules of the same kind have no influence on the velocity of the current with which each of the two gases flow against each other, since there is no loss of momentum of a gas in any direction when two of its molecules collide. Maxwell therefore considered that the correct values to be substituted for L_1 and L_2 in the above formula are the lengths of the free paths of a molecule of one gas among the molecules of the other, so that L_1 and L_2 would be inversely proportional to N_2 and N_1 respectively, and the above expression would be independent of the ratio $\mathrm{N}_1/\mathrm{N}_2$.

The problem at present under consideration deals more particularly with the case in which a very small quantity of one of the gases is present, so that case will be investigated first, by an indirect method which is probably less complicated than that generally used.

2. The determination of the velocity under an electric force and the rate of diffusion of ions into a gas may be investigated by making the ordinary assumptions as to the nature of a collision. It will be seen that the absolute values of the coefficients may be inaccurate, but this does not affect their ratio. For the present, therefore, it will be assumed that the ions travel with a constant velocity of agitation V along free paths of various lengths of mean value l, and that after a collision all directions of motion are equally probable. Also the velocity of the ion due to the electric force is supposed to be small compared with V.

Under these conditions the velocity under an electric force may easily be found. Let m be the mass of an ion, e its charge, then under a force X it travels a distance $s_1 = \frac{1}{2}ft_1^2$ in the time t_1 between the collisions, where $f = \mathrm{X}e/m$. Substituting for t_1 its value l_1/V, then the distance S travelled in the direction X after a number of free paths of lengths $l_1, l_2 \ldots l_n$ have been traversed is

$$\mathrm{S} = \tfrac{1}{2}\frac{f}{\mathrm{V}^2}\cdot(l_1^2+l_2^2+\ldots+l_n^2) = \frac{nfl^2}{\mathrm{V}^2},$$

where l is the mean free path.

The velocity U in the direction of the force becomes $\mathrm{S}/(t_1+t_2+\ldots+t_n)$.

Hence $$\mathrm{U} = \frac{nfl^2}{\mathrm{V}^2(t_1+t_2+\ldots+t_n)} = \frac{fl}{\mathrm{V}} = \frac{\mathrm{X}e}{m}\cdot t,\text{*}$$

where $t = l/\mathrm{V}$ is the average time between two collisions.

[The expression given by Drude† and Thomson,‡ $\frac{1}{2}\frac{\mathrm{X}e}{m}t$, is one-half the correct value obtained under these conditions.]

3. The rate of diffusion of the ions into the gas may be found under similar conditions. It will be supposed that the number of ions is small compared with the number of molecules, and it will therefore be unnecessary to consider the effects of collisions between two ions. A method of investigation which is applicable to this case, and also to the more complicated case in which the effects of collisions are less precisely defined, consists in finding the rate at which the mean square R^2 of the distances of the ions from any point O increases with the time.

When the density of a distribution of ions varies with the distance x from a fixed plane, the number that cross any plane $x =$ const. per second depends

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[*] This formula is also given by P. Langevin, 'Ann. de Chim. et Phys.,' 1903, vol. 28, p. 317.

[†] P. Drude, 'Annalen der Physik,' 1900, vol. 1, p. 566.

[‡] J. J. Thomson, 'Conduction of Electricity through Gases,' second edition, p. 74.

on the rate of variation dn/dx of the number n of ions per cubic centimetre. Hence the mean velocity u of the ions is given by an equation of the form

$$nu = -\mathrm{K}\frac{dn}{dx},$$

where K is the coefficient of diffusion. The gas in which the ions move may be supposed to be at rest since the number of molecules of the gas in any volume is much greater than the number of ions. If this equation be adopted as giving a definition of the rate of diffusion, it is easy to find the value of $d(\mathrm{R}^2)/dt$ in terms of K for any distribution.

If a series of spheres be drawn with O as centre, then the motion with respect to the centre of the ions in the space between two spheres of radii r and $r+dr$ will be the same as if the ions are distributed uniformly in the space between the two spheres. Hence, in dealing with the motion from or towards the centre, the distribution may be considered to be symmetrical with respect to the centre, and the number n per cubic centimetre may be considered as a function of r only.

The value of R^2 is given by the equation

$$\int_0^{r'} 4\pi r^4 n\, dr = \mathrm{R}^2 \int_0^{r'} 4\pi r^2 n\, dr,$$

where the sphere of radius r' extends beyond the region throughout which the ions are distributed so that $n = 0$ and $dn/dr = 0$ when $r = r'$. The integral on the right is constant with respect to the time, being the total number of ions under consideration, so that $d(\mathrm{R}^2)/dt$ is given by the equation

$$\int_0^{r'} r^4 \frac{dn}{dt}\, dr = \frac{d(\mathrm{R}^2)}{dt} \int_0^{r'} r^2 n\, dr.$$

Also the rate at which the number of ions between the spheres r and $r+dr$ is changing is equal to the difference between the rates at which ions are crossing the two boundaries.

Hence $$r^2 \frac{dn}{dt}\, dr = -\frac{d}{dr}(r^2 nu)\, dr = \mathrm{K}\frac{d}{dr}\left(r^2 \frac{dn}{dr}\right) dr.$$

Hence $$\mathrm{K}\int_0^{r'} r^2 \frac{d}{dr}\left(r^2 \frac{dn}{dr}\right) dr = \frac{d(\mathrm{R}^2)}{dt} \int_0^{r'} r^2 n\, dr.$$

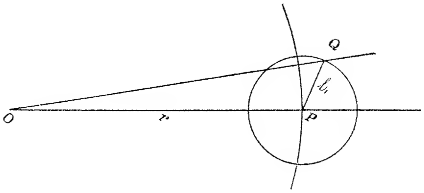
Integrating by parts, the first integral becomes

$$2\mathrm{K}\int_0^{r'} r^3 \frac{dn}{dr}\, dr = 6\mathrm{K}\int_0^{r'} r^2 n\, dr.$$

Hence $$\frac{d(\mathrm{R}^2)}{dt} = 6\mathrm{K}.$$

Hence the rate of variation of the mean square of the distance of any distribution from any point is constant and equal to 6K.

4. The rate of change of the mean square of the distance of any distribution from any point O may also be investigated by considering the actual motion of the particles along their free paths.



Let a number of ions start from a point P, in all directions, with velocity V, so that after a time t_1 they will be distributed uniformly over a sphere of radius $l_1 = \mathrm{V}t_1$.

The mean square of their distances from O is

$$\frac{1}{4\pi l_1^2}\int_0^\pi \mathrm{OQ}^2 \times 2\pi l_1^2 \sin\theta\, d\theta = \tfrac{1}{2}\int_0^\pi (r^2 + l_1^2 + 2rl_1\cos\theta)\sin\theta\, d\theta = r^2 + l_1^2,$$

so that in the time t_1 the mean square of their distances is increased by l_1^2. If the ions collide with molecules after travelling the distance l_1 then all directions of motion become again equally probable, and along the next free path of length l_2 the mean square of the distance increases by l_2^2.

Hence $$\frac{d\mathrm{R}^2}{dt} = \frac{l_1^2 + l_2^2 + \dots}{t_1 + t_2 + \dots} = \frac{2l^2\mathrm{V}}{l} = 2l\mathrm{V} = 6\mathrm{K},$$

where l is the mean free path.

Hence $\mathrm{K} = \frac{1}{3}l\mathrm{V}$.

The ratio of the velocity under unit electric force to the rate of diffusion thus becomes

$$\frac{\mathrm{U}}{\mathrm{K}} = \frac{\mathrm{X}e}{m}\,\frac{l}{\mathrm{V}}\,\frac{3}{l\mathrm{V}} = \frac{3\mathrm{N}e}{m\mathrm{N}\mathrm{V}^2} = \frac{\mathrm{N}e}{\Pi},$$

since $\mathrm{X} = 1$, and $\Pi = \frac{1}{3}m\mathrm{N}\mathrm{V}^2$.

Thus the correct ratio of U/K is obtained when it is supposed that all directions of motion become equally probable after a collision.

5. The question arises whether this definition of a collision is too simple when dealing with an ion moving through a gas. The determinations of the rate of diffusion show that the ions diffuse much more slowly than molecules of gases. Thus ions generated in air diffuse much more slowly than carbonic acid through air, so that presumably the ions have masses associated with them that are large compared with the mass of a molecule. This mass may consist of a group of molecules of the gas attracted by the charge on the ion.

It is necessary therefore to consider whether the above investigation can apply when the masses of the particles diffusing into the gas under consideration are much larger than molecules of the gas.

It is difficult to state exactly how a collision should be specified, but it is obvious that if all directions of motion of a small molecule are equally probable after a collision with a large molecule, the same does not hold for the larger molecule. The particle of large mass will, in general, only be slightly deflected from its original path by an impact with a small mass which may completely reverse the direction of motion of the latter. For the masses m and m' travel with velocities V and V$'$, connected by the equation $m\mathrm{V}^2 = m'\mathrm{V}'^2$, so that the ratio of their momenta is $\sqrt{m}/\sqrt{m'}$. Hence, a transfer of momentum equal to $2m'\mathrm{V}'$ from the larger mass m to the smaller would reverse the direction of motion of the smaller mass, and would have a comparatively small effect on the momentum $m\mathrm{V}$ of the larger mass. If, therefore, there be two sets of molecules, one of which are much larger than the others, and those encounters between molecules are taken into consideration which are such that all subsequent directions of motion of the smaller mass become equally probable, then, when dealing with the motion of the larger masses, it will be necessary to consider that all subsequent directions of motion become equally probable only after several collisions, each collision making a small change in the direction of motion.

In order to calculate the rate of diffusion of the ions or particles of large mass into the gas, the particles, as before, may be considered to move along rectilinear paths of lengths l_1, l_2, etc., with constant velocity V. Let u_1, v_1, w_1 be the components of the velocity along three directions at right angles, during the time t_1 while the particle traverses the first path, u_2, v_2, w_2 the components along the second path, etc. The distances x, y, z which the particle will travel along the axes in the time $t = t_1 + t_2 + \ldots + t_n$ will be

$$x = u_1t_1 + u_2t_2 + \ldots + u_nt_n,$$

$$y = v_1t_1 + v_2t_2 + \ldots + v_nt_n,$$

$$z = w_1t_1 + w_2t_2 + \ldots + w_nt_n,$$

and the square of the distance from the origin of co-ordinates becomes

$$\begin{aligned}\mathrm{R}^2 &= (u_1^2 + v_1^2 + w_1^2)\,t_1^2 + \ldots + 2\,t_1t_2\,(u_1u_2 + v_1v_2 + w_1w_2) + \ldots \\ &= l_1^2 + l_2^2 + \ldots + l_n^2 + 2\,l_1l_2\cos\phi_{12} + 2\,l_1l_3\cos\phi_{13} + \ldots,\end{aligned}$$

where ϕ_{12} is the angle between the first and second path, etc.

The sum of the squares of the free paths being $2nl^2 = 2\,l\,(l_1 + l_2 + \ldots + l_n)$, the expression for R^2 may be written as the sum of n terms, of which the first two are

$$2l_1(l+l_2\cos\phi_{12}+l_3\cos\phi_{13}+l_4\cos\phi_{14}+\ldots),$$
$$2l_2(l+l_3\cos\phi_{23}+l_4\cos\phi_{24}+\ldots).$$

The terms $l_2\cos\phi_{12}+l_3\cos\phi_{13}+\ldots$ are the projections of the second, third, and subsequent paths on the direction of the first path, and their sum has a value λ different from zero, since the angles between the first path and those that immediately follow are small. After a certain number of collisions, having an average value s, the angle ϕ_{1s} becomes equal to $\pi/2$. The average value of the projection of the subsequent paths l_{s+1}, etc., on the first path then becomes zero, since all directions of motion have become equally probable. The n terms in the expression for R^2 then become

$$2l_1(l+\lambda)+2l_2(l+\lambda)+\ldots,$$

where λ is the average distance the ion travels, after a collision, in the direction in which it was moving before the collision. When the number s is small compared with the total number of collisions n under consideration,

$$R^2 = 2(l+\lambda)(l_1+l_2+\ldots+l_n) = 2nl(l+\lambda).$$

Hence $$\frac{dR^2}{dt}=\frac{2nl(l+\lambda)}{t_1+t_2+\ldots+t_n} = 2(l+\lambda)V = 6K.$$

Hence $$K = \tfrac{1}{3}(l+\lambda)V.$$

6. In order to find the velocity U, due to an electric force X, under these conditions, it is to be noticed that, when an ion has velocities u, v, w along the axes before a collision, then, after colliding, it drifts on through distances distances $u\lambda/V$, $v\lambda/V$, and $w\lambda/V$, measured along the axes before all directions of motion become equally probable.

When an electric force acts during a time t_1 while an ion is traversing the path l_1 with a velocity V the distance travelled along the axis of x due to the force X is $\frac{1}{2}ft_1^2$, and, on colliding at the end of the path, the ion has a velocity ft_1 in the direction of the force. The distance the ion travels after the collision due to this velocity is $ft_1\lambda/V$. Hence the total distance S travelled in a time $t_1+t_2+\ldots+t_n$ due to the action of the force, is

$$S = \tfrac{1}{2}ft_1^2+\tfrac{1}{2}ft_2^2+\ldots+\frac{ft_1\lambda}{V}+\frac{ft_2\lambda}{V}+\ldots$$

$$=\frac{f}{V^2}\{\tfrac{1}{2}(l_1^2+l_2^2+\ldots)+\lambda(l_1+l_2+\ldots)\}$$

$$=\frac{f}{V^2}nl(l+\lambda),$$

so that the velocity U under the electric force becomes

$$\mathrm{U} = \frac{\mathrm{S}}{t_1+t_2+\ldots+t_n} = \frac{f}{\mathrm{V}}\,\frac{nl\,(l+\lambda)}{l_1+l_2+\ldots+l_n} = \frac{f\,(l+\lambda)}{\mathrm{V}} = \frac{\mathrm{X}e}{m}\,\frac{l+\lambda}{\mathrm{V}}.$$

The ratio of the velocity to the rate of diffusion $\frac{1}{3}(l+\lambda)\,\mathrm{V}$ is the same as before,

$$\frac{\mathrm{U}}{\mathrm{K}} = \frac{3\,\mathrm{X}e}{m\mathrm{V}^2} = \frac{\mathrm{N}e\mathrm{X}}{\Pi}.$$

7. It is thus seen that the ratio of the velocity under an electric force to the rate of diffusion is independent of the precise definition of the collisions. The question that remains to be decided is the value that must be attributed to l, since l is indefinite when the nature of the collisions remains unspecified, whereas $l+\lambda$ is a perfectly definite quantity, and represents the mean distance that a large number of the particles or ions will travel along an axis if they all start in that direction with a velocity V, when sufficient time is allowed for the motion of agitation to become equally distributed in all directions.

The simplest method of proceeding is to consider the case where two gases A and B are diffusing into each other, n and n' being the number of molecules of the two gases per cubic centimetre. It is obvious that, when n and n' are of the same order of magnitude, the molecules of A collide with each other with a frequency that is of the same order as the frequency of collisions between the molecules of A and B. But, as far as the relative motion of the two gases is concerned, the collisions between the molecules of the same kind can have no effect on the mean velocity of either gas. It may also be seen that such a collision has no effect on the mean square of their distances from a given point, or on the velocity under an electric force. It will be necessary, however, in this case to consider the *mean velocities* u and u' of both gases, so that if K be the rate of diffusion of A, and K′ that of B, then, by definition,

$$\mathrm{K}\frac{dn}{dx} = -n\,(u-u'), \quad \mathrm{K}'\frac{dn'}{dx} = n'\,(u-u'),$$

where K is the rate of diffusion of a small number of molecules of A, as estimated above, that is $\mathrm{K} = \frac{1}{3}\,(l+\lambda)\,\mathrm{V}$, l being the mean free path of a molecule of A in the gas B, when the latter contains n' molecules per cubic centimetre, both l and λ are inversely proportional to n'.

Since $nu+n'u' = 0$, $n'\,(u-u') = (n+n')\,u$, so that the above equations become

$$\frac{\mathrm{K}n'}{n+n'}\,\frac{dn}{dx} = -nu \quad \text{and} \quad \frac{\mathrm{K}'n}{n+n'}\,\frac{dn'}{dx} = -n'u' \quad \text{or} \quad \mathrm{D}\frac{dn}{dx} = -nu.$$

Also, since $n+n'$ is a constant at each point,

$$\frac{dn}{dx} = -\frac{dn'}{dx}.$$

Hence $$\mathrm{K}n' = \mathrm{K}'n.$$

The rate of diffusion of a small number of molecules of A into B when the latter contains $n+n'$ molecules per cubic centimetre is $\frac{\mathrm{K}n'}{n+n'}$, since $\mathrm{K} = \frac{1}{3}(l+\lambda)\mathrm{V}$ and $\frac{n'}{n+n'}(l+\lambda)$ is the value of $(l+\lambda)$ when the number of molecules per cubic centimetre of B is increased from n' to $n+n'$. Hence the rate of diffusion $\frac{\mathrm{K}n'}{n+n'}$, (or D) is independent of the relative values of n and n', and is inversely proportional to the total pressure of the two gases.

Also, since $\mathrm{K}n'/(n+n') = \mathrm{K}'n/(n+n')$, the rate of diffusion of a small number of molecules of A into a gas B, containing a large number $n+n'$ of molecules per cubic centimetre is the same as the rate of diffusion of a small number of molecules of B into the gas A, containing the same number $n+n'$ of molecules per cubic centimetre.

8. In order to find the relative values of the quantities l and λ, as used in sections 5 and 6, it is necessary to define the collisions in some way, for if every trifling deflection of the ion is taken as terminating a free path, then λ will be very large compared with l. The case of a small sphere colliding with a large sphere suggests a convenient method of definition when dealing with ions moving in a gas. When a small sphere collides with a large sphere, and both are perfectly elastic and perfectly smooth, then all directions of motion of the small sphere, after collision, are equally probable. It may therefore be supposed that collisions between the molecules and the ions are such that all directions of motion of the molecule are equally probable after collision. Hence, if l' be the mean free path of a molecule when moving in a gas containing N molecules per cubic centimetre of particles of the same mass and size as the ions, then

$$\mathrm{K} = \tfrac{1}{3}l'\mathrm{V}' = \tfrac{1}{3}(l+\lambda)\mathrm{V},$$

V' being the velocity of agitation of the molecule. The number of collisions per second C between the molecule and the particles, or ions, when there are N of them per cubic centimetre, is equal to the number of collisions per second between an ion and the molecules of the gas, when the latter contains N molecules per cubic centimetre. Hence,

$$l/l' = \mathrm{V}/\mathrm{V}' \quad \text{and} \quad l\mathrm{V}'^2 = (l+\lambda)\mathrm{V}^2 \quad \text{or} \quad \frac{l+\lambda}{l} = \frac{\mathrm{V}'^2}{\mathrm{V}^2} = \frac{m}{m'},$$

where m is the mass of an ion and m' that of a molecule.

Hence $\mathrm{K} = \frac{1}{3}\mathrm{LV}$ and $\mathrm{U} = \frac{\mathrm{X}e}{m}\frac{\mathrm{L}}{\mathrm{V}}$, where $\mathrm{L} = l + \lambda = \frac{lm}{m'}$,

L being the average distance that an ion will travel in the gas when it is projected with a velocity V in a given direction, m the mass of the ion, and m' that of a molecule of the gas, l the mean free path of an ion between collisions with molecules, these collisions being supposed to be of such a nature that all directions of motion are equally probable for the molecule after colliding.

9. Since the mean velocity of ions due to diffusion from places of high density to those of low density is $-\mathrm{K}/n \cdot dn/dx$, the velocity u when an electric force is also acting, is given by the equation

$$u = -\frac{\mathrm{K}}{n}\frac{dn}{dx} + \frac{\mathrm{X}e}{m}\frac{\mathrm{L}}{\mathrm{V}}.$$

Hence $$\frac{1}{\mathrm{K}}nu = -\frac{dn}{dx} + \frac{3n\mathrm{X}e}{m\mathrm{V}^2} \quad \text{or} \quad \frac{1}{\mathrm{K}}(pu) = -\frac{dp}{dx} + n\mathrm{X}e,$$

since p, the partial pressure of the ions, is $\frac{1}{3}mn\mathrm{V}^2$.

This equation, and two similar equations for the y and z directions, are the well-known general equations of motion of particles through a gas, and the above investigations show that they follow immediately from the expressions for the rate of diffusion and the velocity under an electric force, even when *very* improbable assumptions are made with regard to the collisions as shown in section 6, provided that the same assumptions are made in calculating the two quantities that are involved.